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# PATENT SPECIFICATION

(11) 1 396 332

**1 396 332**

(21) Application No. 22421/72 (22) Filed 12 May 1972  
 (31) Convention Application No. 144 340 (32) Filed 17 May 1971 in  
 (33) United States of America (US)  
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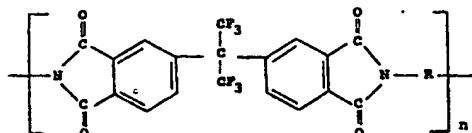
## (54) POLYIMIDE MOULDING COMPOSITIONS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

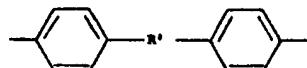
The present invention relates to moulding compositions containing melt-fabricable aromatic linear polyimides.

Polyimides are known polymeric materials and are described in, for example, U.S. Patent Nos. 3,179,631, 3,179,634 and 3,356,648. Also, certain melt-fabricable polyimides are described in U.S. Patent No. 3,234,181. As described in these patents, the polyimides are obtained by reacting specified tetracarboxylic acid dianhydrides with specified diprimary diamines to obtain intermediate polyamide-acids which are converted by any suitable means such as chemical or heat treatment to the corresponding polyimide. The polyimides so obtained are generally intractable materials; however U.S. Patent No. 3,234,181 discloses that melt-fabricable polyimides may be obtained from certain specific tetracarboxylic acid dianhydrides and specific primary diamines. There is no disclosure in the prior art of melt-fusible polyimides derived from a polyamide-acid prepared by reacting 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropene dianhydride with an aromatic primary diamine containing no halogen.

According to the present invention there is provided a moulding composition comprising a filler material and a melt-fabricable linear polyimide having the following structural unit:



wherein R represents m- or p-phenylene, 1,5-naphthylene or



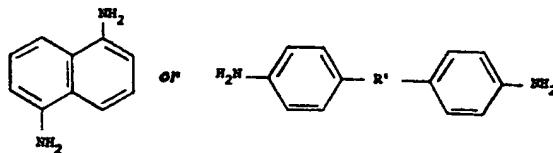
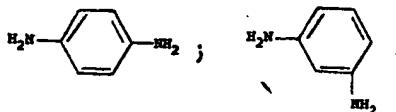
wherein R' represents a divalent bridge which is —O—, —S— or —O—R''—O— where R'' is phenylene, and n is a number sufficient to provide the polyimide with an inherent viscosity of at least 0.15 measured on a solution in sulfuric acid or pyridine of 0.5 gram of the polyimide in 100 ml of solution at 30°C., the polyimide having been prepared by reacting 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropene dianhydride with at least one primary diamine of the formula:

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wherein  $R'$  is as hereinbefore defined, to form a polyamide-acid and converting the polyamide-acid into the polyimide. The polyimide generally has a glass transition temperature of between  $220^\circ\text{C}$ . and  $385^\circ\text{C}$ . When the composition is intended for use in an extrusion or injection moulding process the polyamide-acid preferably has been end-capped with an aromatic anhydride, for example phthalic anhydride, before conversion into the polyamide.

The moulding compositions of the present invention can be moulded into any desired shape, e.g. gears, by conventional compression moulding techniques. Such structures have outstanding physical properties.

The filler materials utilised in the moulding compositions of the invention include, for example, finely divided metals, metal oxides, minerals such as asbestos, abrasive powders such as silicon carbide, graphite powder, diamonds, glass and high temperature resistant resins such as polytetrafluoroethylene. The fillers may be used either separately or in combination in the filled compositions of the invention. The filler can be utilised in the moulding compositions of the invention in amounts up to 80 volume percent, based upon the total volume of the moulding composition.

The intermediate polyamide-acid can be prepared by reacting the 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride with at least one aromatic primary diamine in a suitable solvent at a temperature below about  $75^\circ\text{C}$ . Thereafter, an end-capping agent may be added to the reaction system in order to cap the ends of the polymeric chain, and next the polyamide-acid is converted to the polyimide by a conversion treatment which, for example, may consist of adding a chemical converting agent such as acetic anhydride to the reaction system to cyclise the polyamide-acid to form the imide groups characteristic of the polyimide.

The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride utilised in the process described above may be prepared in the manner described in U.S. Patent No. 3,310,573.

Suitable aromatic primary diamines of the above formula include:

- 4,4'-diamino-diphenyl ether (oxydianiline) (ODA);
- 4,4'-diamino-diphenyl sulfide, (TDA);
- 1,3-bis[4-aminophenoxy]benzene, (RBA);
- 1,4-bis[4-aminophenoxy]benzene,

and any of the aforementioned diamines in combination with each other or in combination with meta-phenylene diamine (MPD); para-phenylene diamine (PPD); 1,5-diamino-naphthalene (1,5-ND). The diamines may be prepared in a manner known per se.

The most desirable procedure for reacting the 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride with the diamine or mixture of diamines includes adding dry solid dianhydride to a pyridine solution of the diamine reactant. Any suitable solvent for the reactants may be used, and satisfactory results have been obtained with pyridine. An important feature of the process is that the pyridine must be dry since any moisture present therein lowers the molecular weight of and decreases the stability of the polymeric product. The solvent may conveniently be dried by passing it through molecular sieves in a manner known per se. The temperature of the reaction solution is maintained below about  $75^\circ\text{C}$ . during the addition of the dianhydride. The dianhydride and the diamine may be reacted in equimolar amounts but it has been found that an excess of the diamine, up to 5.5% on a molar basis, should be used in order to obtain a polyimide having an inherent viscosity of at least 0.30, measured in sulfuric acid as herein defined.

An optional feature of the invention is that wherein the excess diamine end groups of the polyamide-acid are end-capped with an aromatic anhydride such as, for example, phthalic anhydride, in order to obtain satisfactory melt viscosity stability for injection molding and extrusion. A stoichiometric amount of phthalic anhydride end-capping agent is preferably utilized.

Following addition of the end-capping agent, if used, the polyamide-acid is converted to the corresponding polyimide, for example by adding acetic anhydride. The acetic anhydride dehydrating agent may be used in amounts of between 2 and 8 moles per mole of polyimide polymer produced. The resulting polyimide precipitates upon addition to a stirred miscible non-solvent such as, for example, methanol, and may be recovered by known means such as filtration and, preferably, the polyimide is thereafter washed and dried.

A unique feature of the composition of the present invention is the very high loading of filler material that can be incorporated therein to provide useful articles having high temperature resistance properties. While most known polyimides can be filled with low concentrations of filler materials such as described hereinabove, the incorporation into such polyimides of very high concentrations of fillers results in a severe reduction in physical properties such as tensile strength of molded articles prepared therefrom. It is believed that the deterioration of properties of such polyimides is due to the lack of melt flow properties of the polyimides which prevents the polyimides from filling the many voids which exist in moldings prepared from compositions containing a high loading of fillers. The composition of the present invention is unique in that the specific class of polyimide therein is characterized by a high degree of melt-fabricability which renders possible the preparation of highly filled moldings that have tensile strengths in excess of 1500 psi and even in excess of 3000 psi at filler loadings exceeding 60 volume percent.

The polyimide compositions derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride may be compression molded by adding the composition in powder form into a chase and placing top and bottom closure plates on the chase and inserting the entire assembly into a hydraulically operated press. The mold is heated and maintained at a temperature of between 370°C. and 425°C. and a pressure of at least 1000 psi is applied to the mold, and the mold is thereafter allowed to cool to below 100°C. while under pressure after which the mold is removed.

The invention will now be illustrated by reference to the following Examples. All parts and percentages expressed in the Examples are by weight unless otherwise indicated.

The polymers and shaped structures thereof prepared in the following Examples were evaluated in accordance with the following procedures:

**INHERENT VISCOSITY** — The inherent viscosity of the polymer samples was obtained by measuring the viscosity of both the polymer solution and the solvent, and inherent viscosity was calculated from the following equation:

$$\text{Inherent Viscosity} = \frac{\text{Natural Logarithm (Viscosity of Polymer Solution)}}{(\text{Viscosity of Solvent})} - C$$

where C is the concentration expressed in grams of polymer per 100 milliliters of solution. The polymer solution was obtained by dissolving 0.5 gram of the polyimide polymer in an initial amount of solvent less than 100 mls. at 30°C., and then adjusting the total solution to 100 mls. by adding additional solvent at 30°C. The solvents used were either pyridine or sulfuric acid, as indicated with the reported values of inherent viscosity herein. As is known in the polymer art, inherent viscosity is related to the molecular weight of the polymer.

**GLASS TRANSITION TEMPERATURE, Tg** — The glass transition temperature of the polymer samples was obtained by either differential scanning calorimetry or differential thermal analysis techniques at 30°C./min. using a Du Pont Model 900 DTA Analyzer. The glass transition temperature was defined as the point of intersection of the intersecting tangent lines at the point of first inflection of the heating curve of the polymer.

**NOTCHED IZOD — ASTM—D 256**

**TENSILE PROPERTIES** — Tensile properties such as tensile strength, tensile modulus and elongation were measured in accordance with ASTM—D 1708.

**MELT FABRICABLE POLYIMIDE** — The polyimides utilized in the Examples may be prepared in accordance with the following procedure:

To a 3 liter 3-neck round bottom flask equipped with a thermometer, mechanical stirrer, condenser and nitrogen purge is added 100.06 g. (0.5003 mole, 4% excess) 4,4'-diaminodiphenyl ether (ODA). The diamine is washed with 700 ml. of distilled pyridine which has been dried over molecular sieves just prior to use. The mixture is stirred and heated to 50—60°C. to effect solution of the diamine. 213.6 g. (0.4811 mole) of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropene dianhydride (hereinafter called 6F) is then added as a dry solid in small portions over about five minutes with stirring. Last traces are washed in with 100 ml. dry pyridine. The temperature is maintained at 50—60°C. At the end of 45 minutes all of the dianhydride is in solution and 5.6962 g. (0.03849 mole) phthalic anhydride capping agent is added all at once and washed in with 100 ml. dry pyridine. At this point the temperature of the solution is 40—50°C. After stirring for 45 minutes all of the phthalic anhydride is in solution and 313 ml. of acetic anhydride is added slowly through the top of the condenser. The temperature of the reaction mixture rises from 39°C. to 55°C. Imidization occurs essentially instantaneously. After stirring for at least 30 minutes the solution of 6F/ODA polyimide is cooled to room temperature and poured with vigorous stirring into a Waring blender partly filled with a non-solvent, e.g., methanol. The granular polymer which comes out of solution is separated by filtration, washed with about 500 ml. methanol, and dried overnight in a vacuum oven at 120—170°C. It is finally dried for at least two hours at 260°C. to remove last traces of water and solvents. The product is characterized by having an inherent viscosity of 0.42, as measured in sulfuric acid at 30°C.

#### EXAMPLE 1.

To a 2 liter 3-neck round bottom flask equipped with a thermometer, mechanical stirrer and water cooled condenser was added 590 ml. pyridine and 195 g. 6F/ODA polyimide (Inh. Vis. = 0.36 in sulfuric acid) end-capped with phthalic anhydride. The mixture was stirred with refluxing until all polymer was dissolved. The solution was then transferred to a one quart size can and stirred using a "Cowles" mixer. To the stirred solution 26 g. (10 wt.%) of "Teflon" 7C TFE fluorocarbon resin and 39 g. (15 wt.%) of graphite ("Dixon" Airspun #20009) were slowly added and the mixture allowed to stir for 6 minutes. The mixture was then poured slowly into a large excess of methanol (run in two portions in 1500 cc methanol each time) and stirred in a Waring blender to precipitate out the polyimide. The product was separated by filtration and washed with two volumes of methanol. It was dried in a vacuum oven at 150°C. under nitrogen overnight. The product mixture had a melt flow at 390°C. of 0.18 g./min.

Samples of polymer were compression molded at 375°C. and a pressure of 4160 psi. The following properties were measured in microtensile bars machined from the compression molded disc:

Tensile Strength = 7800 psi  
 Tensile Modulus = 764,000 psi  
 Elongation = 1.7%

The coefficient of linear thermal expansion was also measured (ASTM E—228) and found to be  $4.0 \times 10^{-5}$  in./in./°C.

A wear disc was machined and tested and was found to have wear factors of

$$\frac{167 \times 10^{-10} \text{ and } 189 \times 10^{-10}}{\text{ft.lb.hr.}} \text{ cu.in.min.}$$

50 by weight and by thickness, respectively. These values compare with

$$\frac{8400 \times 10^{-10} \text{ and } 8500 \times 10^{-10}}{\text{ft.lb.hr.}} \text{ cu.in.min.}$$

by weight and by thickness, respectively for an unfilled 6F/ODA control (Inh. Visc. = 0.43 in sulfuric acid).

The wear test is described in the following reference — Lewis, R. B., "Mech. Eng." 86, 32—35 (1964). ("COWLES", "TEFLON" and "DIXON" are Registered Trade Marks)

**EXAMPLE 2.**

5 A. Preparation of Thermopolymerizable 6F/ODA polyimide Water "Short-Stopping" Method

To a 3 liter 3-neck round bottom flask equipped with a mechanical paddle stirrer, thermometer, water cooled condenser and nitrogen blend was added 213.6 g. (0.4811 mole) of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (hereinafter referred to as 6F) and 750 cc pyridine. The mixture was heated with stirring to 65°C. to effect solution. 1.04 ml. (0.0577 mole, 12 mole% based on the 6F dianhydride) of water was added and stirring continued at 65°C. for 5 minutes. Then, 96.22 g. (0.4811 mole) of ODA was added slowly maintaining the pot temperature at 66—69°C. by means of a water-icing bath. The ODA was washed in with 150 cc pyridine. Stirring was continued for 45 minutes. The polyamide-acid solution was then cooled to about 37°C. and 300 cc. acetic anhydride was added to bring about imidization. The temperature rose to 54°C. due to the exothermic heat of reaction. Stirring was continued for 30 minutes. The polyimide solution was then cooled to room temperature, diluted with an additional 500 cc. pyridine to reduce solution viscosity and precipitated by adding slowly to an excess of methanol stirred in a Waring blender. The slurry was filtered and the finely divided polymer was washed with 2 volumes of methanol and dried in a vacuum oven at 150°C. under nitrogen. The product (267.3 g.) had an inherent viscosity (pyridine) of 0.25.

25 The following physical properties were measured on polymer made in the above manner and having an initial inherent viscosity (pyridine) of 0.24. Compression molding was carried out at 400°C. and 4160 psi with a 15 minute hold-up at temperature and pressure.

Tensile Strength = 14,200 psi  
 % Elongation = 6.7  
 Notched Izod  
 Impact = 0.9 ft.lb/in.

30 The thermopolymerizable nature of the polymer was demonstrated by the fact that after 5 minutes at 400°C. under a nitrogen atmosphere the inherent viscosity (pyridine) increased from 0.24 to 0.36. After 10 minutes exposure at this temperature the polymer would not dissolve even in boiling pyridine but only underwent swelling to produce a gelatinous mass.

35 B. Preparation Thermopolymerizable 6F/ODA polyimide — Asbestos Composition

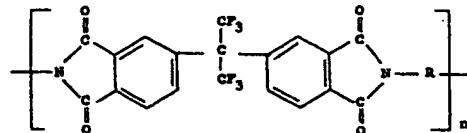
A dry blend consisting of 15 weight percent thermopolymerizable 6F/ODA polyimide prepared as above (inherent viscosity pyridine of 0.24) and 85 weight percent of an 80/20 mixture by weight of Carey Canadian and "Noramite" (Registered Trade Mark) asbestos was prepared and compression molded at 400°C. and 12,700 psi. The composition had a tensile strength of 400 psi.

40 C. For comparative purposes the procedure in B above was repeated for preparing compression molded articles utilizing 15 weight percent of a polyimide powder derived from 3,4,3',4'-benzophenone tetracarboxylic acid dianhydride and oxydianiline (ODA) prepared in accordance with U.S. 3,179,631. The dry blended mixture of polyimide powder and asbestos was molded at 440°C. and a pressure of 25,000 psi. The molding was of poor quality and had a tensile strength of less than 100 psi.

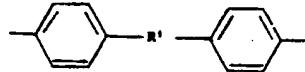
45 D. Comparative Example C above was repeated utilizing a polyimide powder derived from pyromellitic dianhydride (PMDA) and oxydianiline (ODA). The sample was molded at 440°C. and at a pressure of 22,000 psi. The molding was of poor quality and had a tensile strength of less than 100 psi.

50 **WHAT WE CLAIM IS:—**

55 1. A molding composition comprising a filler material and a melt-fabricable linear polyimide having the following structural unit:

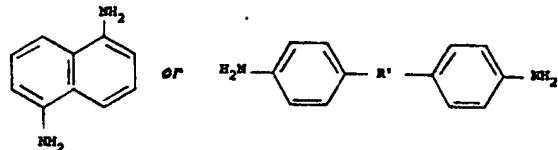
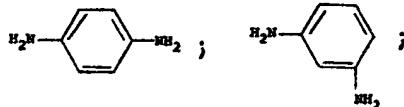


wherein R represents m- or p-phenylene, 1,5-naphthylene or



5 wherein R' represents a divalent bridge which is —O—, —S— or —O—R''—O— wherein R'' is phenylene, and n is a number sufficient to provide the polyimide with an inherent viscosity of at least 0.15 measured on a solution in sulfuric acid or pyridine of 0.5 gram of the polyimide in 100 ml of solution at 30°C., the polyimide having been prepared by reacting 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride with at least one primary diamine of the formula:

5



10 wherein R' is as hereinbefore defined, to form a polyamide-acid and converting the polyamide-acid into the polyimide.

10 2. A molding composition according to claim 1 wherein the polyamide-acid has been converted into the polyimide by the use of acetic anhydride.

15 3. A molding composition according to claim 1 or 2 wherein the polyamide-acid has been end-capped with an aromatic anhydride before conversion into the polyimide.

15 4. A composition according to any one of claims 1 to 3 wherein the filler material comprises up to 80 moldable volume percent, based upon the total volume of moldable filler material in the composition.

20 5. A composition according to any one of the preceding claims wherein the filler material is a finely divided metal, metal oxide or mineral.

20 6. A composition according to any one of claims 1 to 4 wherein the filler material comprises an abrasive powder.

25 7. A composition according to claim 6 wherein the abrasive powder is silicon carbide or diamond.

25 8. A composition according to any one of claims 1 to 4 wherein the filler material is polytetrafluoroethylene.

25 9. A composition according to any one of claims 1 to 4 wherein the filler material is graphite.

30 10. A composition according to claim 1 substantially as described in any one of the Examples.

30 11. A molded article obtained from a composition as claimed in any one of the preceding claims.

30 12. An article according to claim 11, wherein the filler material comprises up to 80 volume percent of the moldable material in the article.

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